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QUALITATIVE ASPECTS OF AN INDUCTIVELY COUPLED PLASMA IN THE SPE--ETC(U)

JAN 80 D R HEINE, J S BABIS, M B DENTON N00014-75-C-0513

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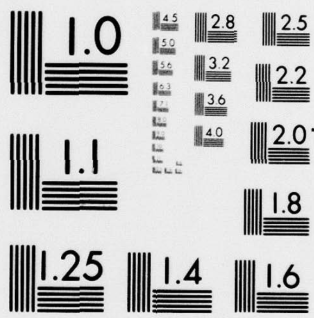

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Contract N00014-75-C-0513
Task No. NR 051-549

9 Interim Technical Report No. 23

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QUALITATIVE ASPECTS OF AN INDUCTIVELY COUPLED PLASMA IN THE SPECTRAL REGION BETWEEN 120 AND 185 nm.

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by

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Prepared for Publication

in

Applied Spectroscopy

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: 23	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): QUALITATIVE ASPECTS OF AN INDUCTIVELY COUPLED PLASMA IN THE SPECTRAL REGION BETWEEN 120 and 185 nm	5. TYPE OF REPORT & PERIOD COVERED: INTERIM
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): D. R. Heine, J. S. Babis, and M. B. Denton	8. CONTRACT OR GRANT NUMBER(s): N00014-75-C-0513
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of Arizona, Tucson, Arizona 85721	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 051-549
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Arlington, Virginia 22217	12. REPORT DATE: January, 1980
	13. NUMBER OF PAGES: 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Applied Spectroscopy.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Inductively Coupled Plasma, Vacuum Ultraviolet Emission Spectra, Oxygen, Nitrogen, Bromine, Chlorine, Sulfur, Carbon

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Investigations of the atomic emission lines produced by a variety of non-metals in the vacuum ultraviolet spectral region are reported. A number of promising analytical lines for oxygen, nitrogen, carbon, bromine, sulfur, and chlorine were observed between 120 and 185 nm using both photographic and electronic detection. A unique experimental configuration employing a side-arm torch which directly couples to the vacuum spectrometer/spectrograph is described.

Qualitative Aspects of an Inductively Coupled Plasma

in the Spectral Region between 120 and 185 nm

by

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Abstract

Investigations of the atomic emission lines produced by a variety of non-metals in the vacuum ultraviolet spectral region are reported. A number of promising analytical lines for oxygen, nitrogen, carbon, bromine, sulfur, and chlorine were observed between 120 and 185 nm using both photographic and electronic detection. A unique experimental configuration employing a side-arm torch which directly couples to the vacuum spectrometer/spectrograph is described.

Index Headings: Inductively Coupled Plasma, Vacuum Ultraviolet Emission Spectra, Oxygen, Nitrogen, Bromine, Chlorine, Sulfur, Carbon.

INTRODUCTION

Although inductively coupled plasmas (ICP) have become increasingly more popular in recent years, few investigations have been conducted in the spectral region below 200 nm, primarily due to the difficulties encountered in observing emissions in the vacuum ultraviolet (VUV) region. The principle problems result from the absorption by molecular oxygen in the atmosphere below 185 nm, necessitating the use of a non-absorbing gas or a vacuum in the optical path, and the diminished transmission of quartz below 200 nm. In addition, most common spectrometers and photomultiplier tubes are not readily usable at wavelengths less than 180 nm, due to problems associated with purging and optical efficiency.

Several features of this region, however, make it attractive to investigate. According to wavelength tables there are many atomic emission lines from elements which do not have very many or very strong lines in the ultraviolet-visible region, including bromine, chlorine, sulfur, nitrogen, and oxygen (1,2). Kirkbright, et al have studied the ICP excited emission from sulfur, phosphorous, iodine, arsenic, selenium, and mercury at wavelengths as short as 170 nm (3,4). Useful analytical emission lines from each of these elements were observed in the vacuum ultraviolet region. Detection limits were in the ppm range or better. Ellebracht, et al have made similar investigations using a dc discharge plasma (5,6). However, it appears that no examinations at wavelengths shorter than 170 nm have been reported with an ICP.

In this manuscript a high power inductively coupled plasma is described, including a unique torch design providing coupling to a vacuum spectrometer. The relative intensities and wavelengths for the emission lines observed from oxygen, nitrogen, carbon, sulfur, chlorine, and bromine between 120 and 185 nm are presented.

I. EXPERIMENTAL

A. Apparatus. The ICP system (Figure 1) consists of a Collins Radio (Cedar Rapids, IA) 204C-1 linear power amplifier modified to operate at 27.12 Mhz. This unit has a rated power output capability of 10 Kw peak envelope power. The external excitor driving the power amplifier employs a Hi-Ox 27.12 Mhz crystal oscillator, a PAX-1 amplifier (International Crystal Manufacturing, Oklahoma City, OK), and a one watt class C amplifier. These stages are contained in a small, electrically-shielded enclosure located inside the power amplifier cabinet. Rf output power is controlled by adjusting the dc voltage (0-15 volts) applied to the second two stages of the excitor. The adjustable voltage supply is interfaced to a MITS (Albuquerque, NM) Altair 8800 micro-computer for computer control of the output power.

The matching network and torch design have been described previously (7). These two components are enclosed in an 46 cm x 46 cm x 38 cm deep metal box and are attached to a pair of Velmex, Inc. (East Bloomfield, NY) dovetail slides for horizontal and vertical movement of the torch assembly perpendicular to the viewing axis. The location of the plasma torch is controlled by a Denco Research, Inc. (Tucson, AZ) SM-2A Stepper Motor Controller System, interfaced to the micro-computer.

The nebulizer used for aqueous samples is a modified Babington principle nebulizer previously reported (8).

For introduction of gases and volatile organic liquids into the plasma, the Babington nebulizer was replaced with a rotameter and liquid head-gas sampling bottle. Argon sample gas flow was adjusted to approximately 1 lpm using a Veriflo Corp. (Richmond, CA) model SC440HF flow controller and subsequently introduced into one arm of a Crawford Fitting Co. (Solon, OH) Swagelok 6.35 mm (1/4") brass tee. A slow flow rate of analyte gas was measured with a Matheson (East Rutherfored, NJ) model 7641 flowmeter unit containing a #602 flowmeter tube, and subsequently introduced into a second arm of the tee, with the third arm connected to the plasma torch sample tube. The analyte gas flow rates were between 2-10 ml/min. (2-20 mg/min), which was sufficient to produce good spectra. To sample volatile organic liquids, 2-3 ml of the sample were placed in a small head-gas sampling bottle, located between the Swagelok tee and the flow meter.

A unique coolant tube (Figure 2) which allows direct viewing of the discharge without requiring observation through quartz or the atmosphere was used in this study. A 25 mm o.d. side-arm on the coolant tube just above the rf load coil attaches to the vacuum spectrometer through a 22 cm length of 26 mm o.d. copper tube as shown in Figure 3. Two variations of the coolant tube were successfully utilized. The coolant tube expands from 20.5 to 25 mm o.d. just above the load coil where the side-arm is joined, in the configuration shown in Figure 2. The other geometry uses a straight 20.5 mm o.d. quartz tube with a 25 mm side-arm, depicted in Figure 3. During operation of the ICP, the side-arm was constantly flushed between the CaF_2 window and the plasma discharge with 0.3-0.5 lpm of helium. Helium was chosen instead of argon or nitrogen because of its greater optical transparency at shorter wavelengths.

A Jarrell-Ash (Newtonville, MA) model 78-651 one-half meter Seya-Namioka mount scanning vacuum spectrometer was used in this work, with either film or a photomultiplier tube as the detector. The entrance slits were approximately 54 cm from the center of the plasma discharge; the exit slits were replaced with a film holder for spectrographic observations. The vacuum inside the spectrometer was maintained at 10^{-4} torr or better for all studies.

All spectra recorded on film were taken with 100 μm entrance slits on Eastman Kodak (Rochester, NY) SWR Film, emulsion number SP764. Strip chart recordings of the developed film were made with a Perkin-Elmer (Norwalk, CT) 1010A PDS Microdensitometer contolled by a Data General Corp. (Southboro, MA) Eclipse S-130 minicomputer.

For scanning studies, the film holder was replaced with an exit slit assembly. Both entrance and exit slit widths were adjusted to 150 μm for detection with a Gencom, Inc. (Plainview, NY) EMI G-26E315 photomultiplier tube which has a spectral response from 110-220 nm. This tube was operated at 3 kV supplied by a Carad Corp. (Palo Alto, CA) model 1522B High Voltage Precision Power Supply. The output current was amplified with electrometer using a Signetics Corp. (Sunnyvale, CA) NE/SU 536 FET Input Operational Amplifier. The amplified signal was recorded on a Linear Instrument Corp. (Irvine, CA) 255/MM strip chart recorder. Typical operating conditions are listed in Table I.

B. Reagents. All gases were commercial grade used without further purification except the 1% fluorine in argon, which was supplied by Matheson (East Rutherford, NJ).

All reagents were Mallinckrodt Chemical Works (St. Louis, MO) AR grade used without further purification. Aqueous samples were prepared in distilled deionized water.

II. RESULTS AND DISCUSSION

A. Torch Operation. Operation and performance of the special plasma torch used in this work was not significantly different from conventional torch designs. The discharge was tear-drop shaped and symmetrical except for a flat spot resulting from the low flow of helium from the side-arm. Argon support gas flow rates were unchanged (see Table I). Power levels between 750 watts and 4 kilowatts have been successfully used with this torch design. Data for this work, however, was collected at power levels between one and two kilowatts.

B. Spectral Results. Representative spectra of several elements, derived from film data, are shown in Figure 4. Exposure times of the films varied from 10 seconds to 5 minutes, depending on the complexity and detail desired. Nearly identical spectra were achieved using the photomultiplier tube by scanning the wavelength, although resolution was less because wider slits were used.

A listing of observed spectral lines, their source, and relative intensities is presented in Table II. The wavelengths were taken from literature values (1,2). Relative interelement intensities of emission lines were determined using photomultiplier tube data because of nonlinear film behavior, though in many cases agreement between the two types of detectors was very good.

The background spectrum of argon, Figure 4a, shows five distinct peaks, all due to impurities in the argon gas. Oxygen has an intense triplet at 130 nm which is listed as a_1. Nitrogen appears at both 149 nm, a_2, and at 174 nm, a_5. Peak a_2 is an unresolved triplet and a_5 is a doublet which is partially resolved. Carbon multiplets are responsible for the remaining two emission lines seen in the background spectra. Peak a_3 is a quartet at 156 nm and a_4 is a sextet at 165 nm.

Fifteen emission lines were observed for bromine, Figure 4b, with several that appear very promising for quantitative analysis, viz. 153.17 nm, 163.34 nm, and the 157 nm doublet. This particular spectrum was taken by aspirating a dilute solution of $Br_2(aq)$ into the discharge; identical spectra were also observed by placing a few drops of Br_2 in the head-gas sampler as described in the experimental section.

Sulfur has many intense emission lines in the VUV. Figure 4c is the spectrum obtained by aspirating a dilute solution of $CrSO_4$ into the plasma discharge. Intensity measurements were obtained by aspirating CS_2 and recording the response of the photomultiplier tube as a function of the wavelength. The results in Table II indicate that the 180.73 nm line is the most sensitive, closely followed by the 166.67 nm line and the 182 nm doublet.

The chlorine spectrum in Figure 4d, obtained by aspirating a dilute solution of HCl into the discharge, has several strong emission lines from

Cl (I). The most intense lines of chlorine are observed at 133.57 nm, 134.72 nm, and 135.17 nm.

A 1% fluorine in argon gas mixture was used as an analyte gas to investigate the emission of fluorine in the VUV. No emission lines were observed from fluorine in the spectral region between 120 nm and 185 nm.

III. CONCLUSIONS

The VUV region holds great potential for elemental analysis with an ICP. Sensitive lines for many non-metallic elements have been identified and warrant quantitative investigation.

Previous investigations have reported the use of an ICP as a detector for gas chromatographic effluents but were unable to detect the presence of nitrogen and oxygen in the spectral region employed (9, 10, 11). The additional information available in the vacuum ultraviolet region should significantly enhance the capabilities of ICP-GC detection. This should also be important in other applications, such as ICP-liquid chromatography in which detection of non-metals is desirable.

ACKNOWLEDGEMENTS

This research was partially supported by the Office of Naval Research and by an Alfred P. Sloan Foundation Research Fellowship awarded to M. B. Denton.

TABLE I. Typical operating parameters.

Frequency	27.12 Mhz; crystal controlled
Power	0.75 - 4 kW forward power
	<20 watts reverse
Argon flow rates	
Coolant	12 - 20 lpm (depending on power)
Auxiliary	0 - 2 lpm (depending on power)
Sample	1 lpm
Helium side-arm flow	0.3 - 0.5 lpm
Slit widths	
Film detector	100 nm
PMT detector	150 nm
PMT voltage	3.0 kV
Amplifier gain	20 na in = 1 volt out (max)

TABLE II. Wavelengths and relative intensities of observed emission lines.

Element	Wavelength (nm)	designation fig. 4	relative intensity[a,b]
Oxygen	130.22, 130.49, 130.60	a_1	100.0
Nitrogen	149.26, 149.28, 149.47	a_2	100.0
	174.27	a_5	72.0
	174.52	a_5	35.0
Carbon	145.90, 146.33	c_8	22.6
	154.15, 154.22, 154.40, 154.52	c_{12}	1.4
	156.03, 156.07, 156.13, 156.14	a_3	70.7
	165.63, 165.69, 165.70 165.74, 165.79, 165.81	a_4	100.0
	175.18	c_{15}	4.7
	193.10	...[c]	1.2
Bromine	124.96	b_1	0.5
	125.58	...[c]	<0.5
	125.92	b_2	0.5
	126.62	...[c]	<0.5
	127.95	b_3	1.0
	128.63	...[c]	<0.5
	131.67, 131.74, 131.77	b_4	2.8
	138.46	b_5	3.0

	144.99	b_6	5.6
	148.85	b_7	16.5
	153.17	b_8	50.0
	154.06	b_9	35.7
	157.48, 157.64	b_{10}	100.0
	158.23	b_{11}	30.4
	163.34	b_{12}	71.4
Sulfur	126.92, 127.08	c_1	10.0
	128.01	c_2	2.7
	131.65, 131.66	...[c]	1.8
	132.66	c_3	14.7
	138.16, 138.55	...[c]	0.9
	140.93	c_4	1.6
	141.29	c_5	3.6
	142.50, 142.52	c_6	25.5
	143.32, 143.33	c_7	28.2
	147.30, 147.40, 147.44, 147.46	c_9	63.0
	148.16, 148.17, 148.32, 148.35	c_{10}	30.0
	148.56, 148.71	c_{11}	13.1
	166.67	c_{14}	90.9
	180.73	...[c]	100.0
	182.03, 182.64	...[c]	81.8
Chlorine	133.57	d_4	47.4
	134.72	d_5	100.0
	135.17	d_6	59.9

136.34	d_7	19.8
137.95	d_8	2.6
138.98	d_9	11.4
139.65	d_{10}	7.8
148.17	d_{14}	...[d]

[a]Intensity of line relative to strongest line of each element in spectral region investigated.

[b]Uncorrected for the non-linearity of PMT response with respect to wavelength.

[c]Obtained from data not presented in figure 4.

[d]Shoulder, intensity not measurable.

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Figure Captions

Figure 1. Inductively coupled plasma system.

Figure 2. ICP Torch assembly with side-arm coolant tube. Note that this demountable assembly provides the capability of rapid interchange of quartz tube configurations.

Figure 3. Vacuum spectrometer with adapter and torch assembly: a, load coil; b, side-arm; c, O-rings; d, purge gas inlet; e, shutter; f, CaF_2 window, 2 mm x 19 mm dia; g, slit assembly; h, grating; i, PM Tube; j, 22 cm copper tube.

Figure 4. Representative spectra: a, background spectrum; b, bromine; c, sulfur; d, chlorine.

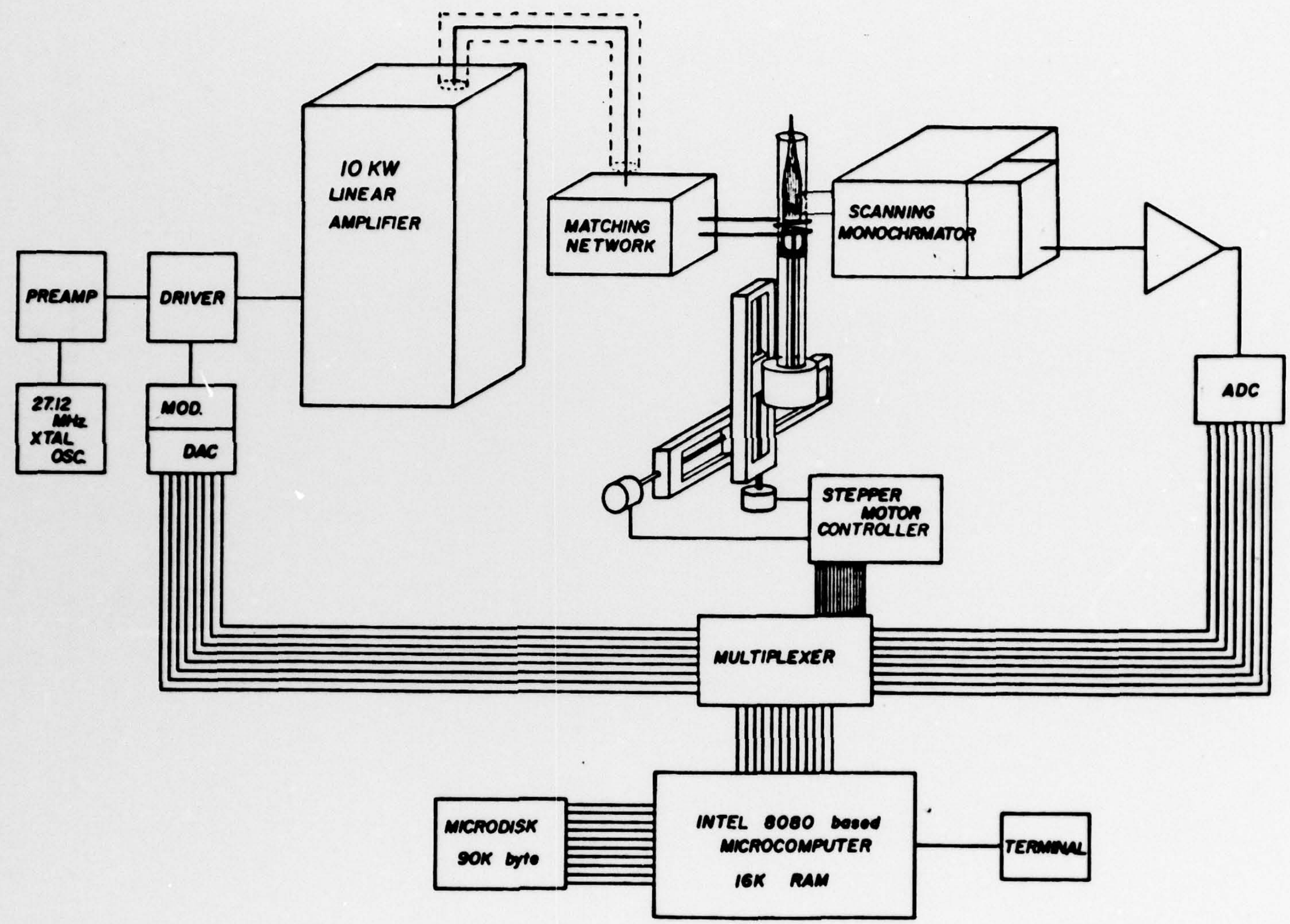
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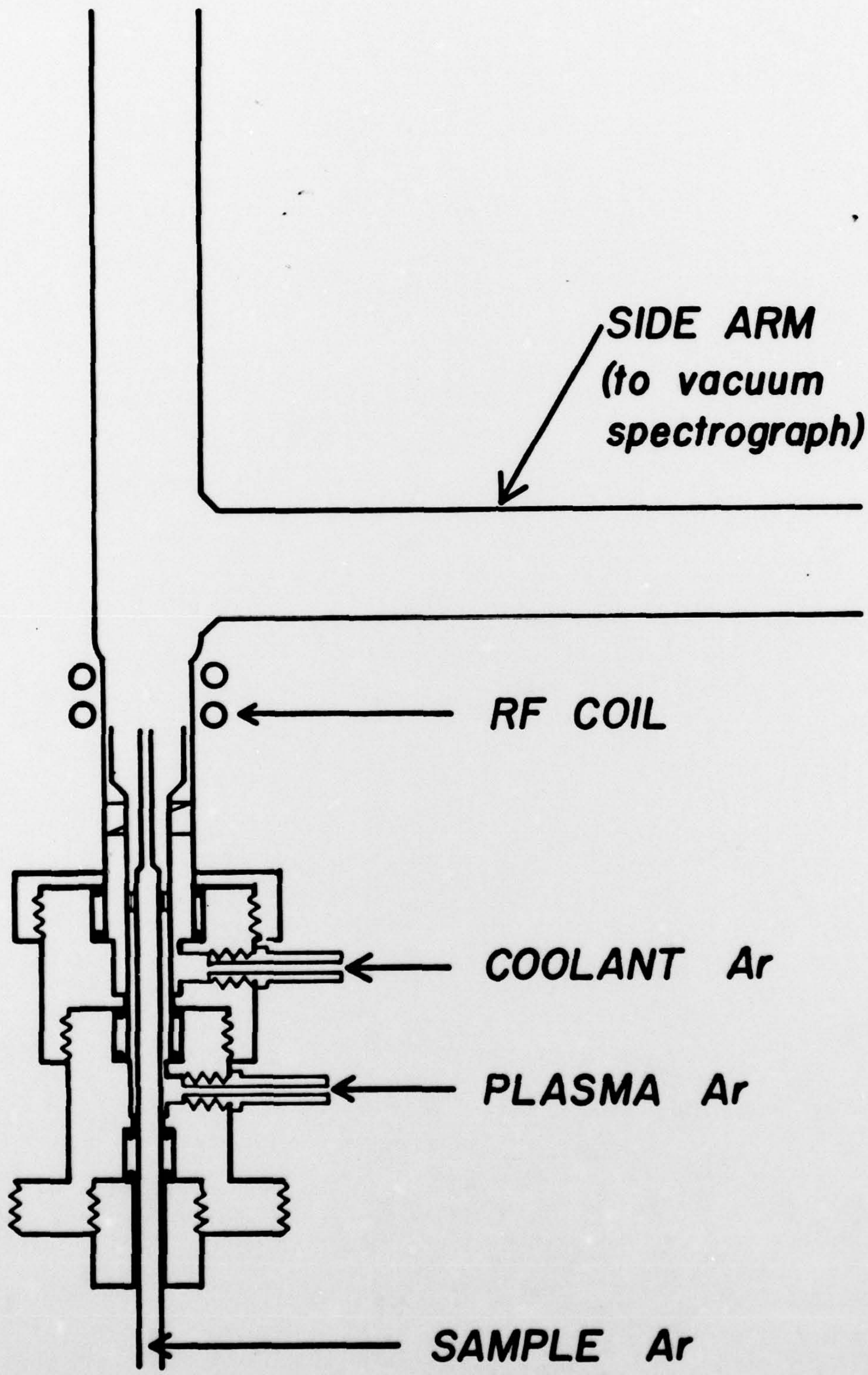
Figure 1.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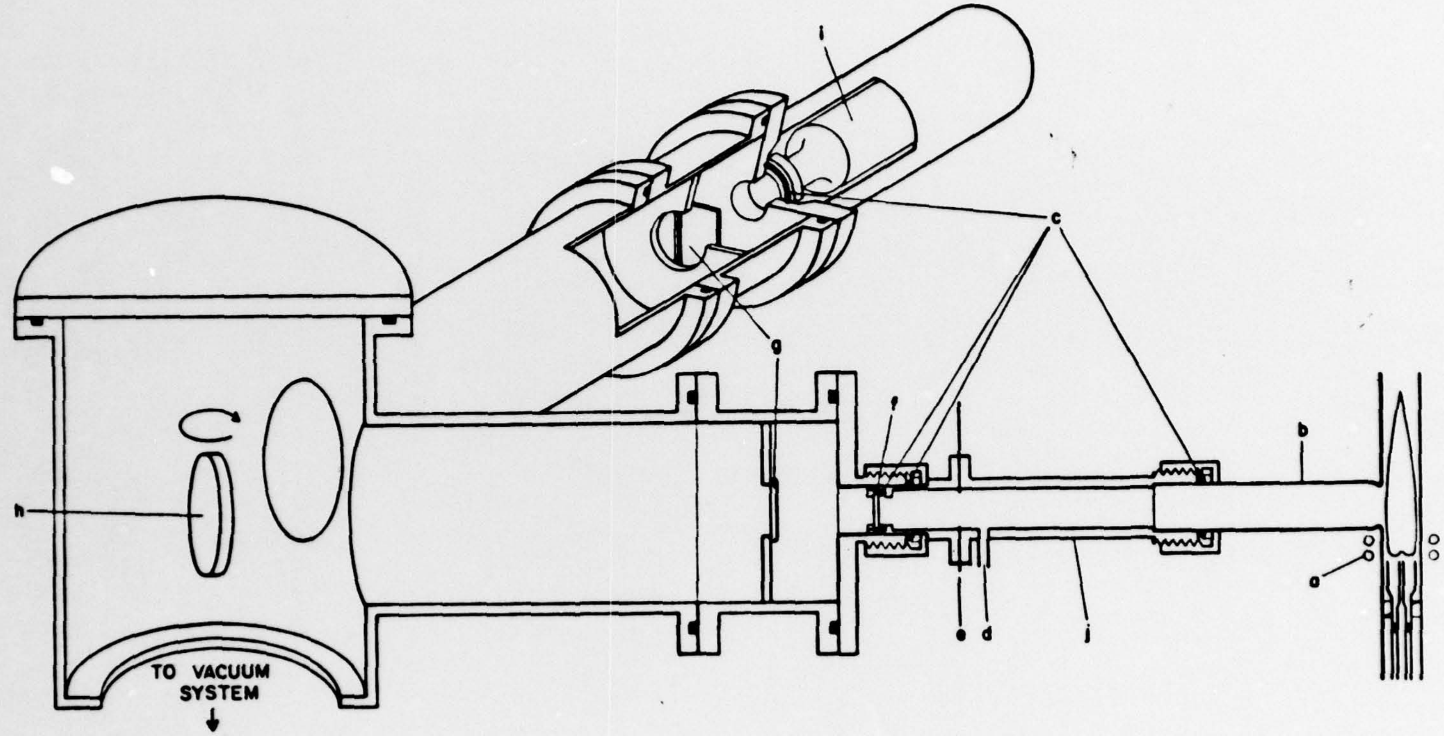
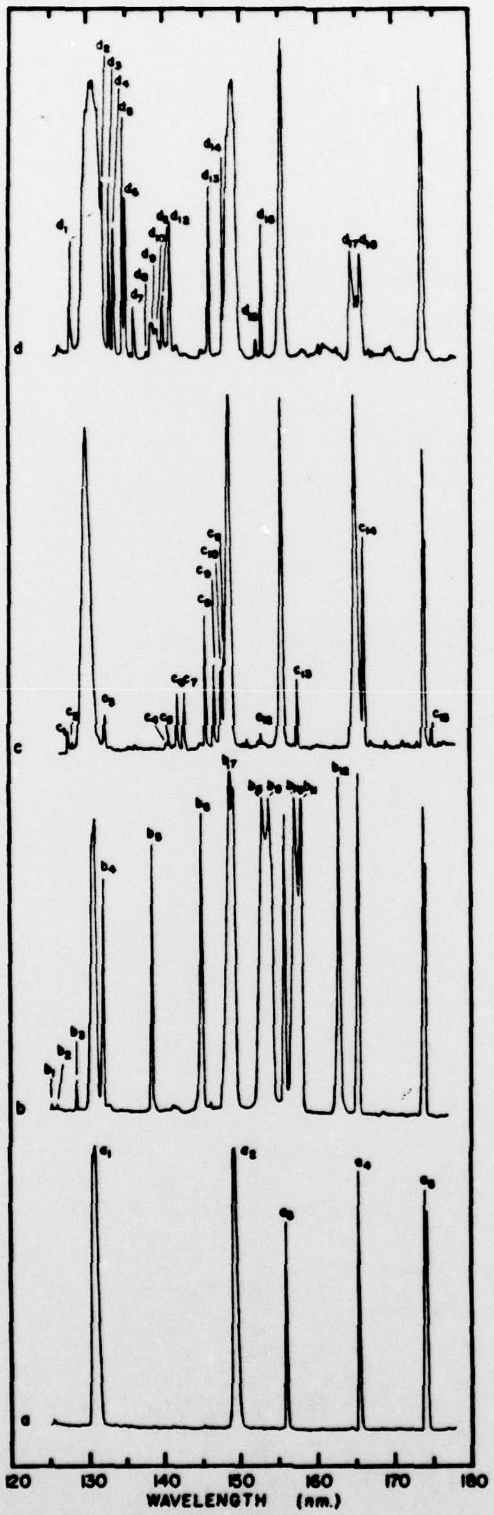


Figure 3.



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